Submitted to Ap.J.

Calculations of the Far-Wing Line Profiles of Sodium and Potassium in the Atmospheres of Substellar-Mass Objects

Adam Burrows[1], Maxim Volobuyev[1,2]

ABSTRACT

At the low temperatures achieved in cool brown dwarf and hot giant planet atmospheres, the less refractory neutral alkali metals assume an uncharacteristically prominent role in spectrum formation. In particular, the wings of the Na-D (5890 Å) and K I (7700 Å) resonance lines come to define the continuum and dominate the spectrum of T dwarfs from 0.4 to 1.0 μm. Whereas in standard stellar atmospheres the strengths and shapes of the wings of atomic spectral lines are rarely needed beyond 25 Å of a line center, in brown dwarfs the far wings of the Na and K resonance lines out to 1000's of Å detunings are important. Using standard quantum chemical codes and the Unified Franck-Condon model for line profiles in the quasi-static limit, we calculate the interaction potentials and the wing line shapes for the dominant Na and K resonance lines in H_2- and helium-rich atmospheres. Our theory has natural absorption profile cutoffs, has no free parameters, and is readily adapted to spectral synthesis calculations for stars, brown dwarfs, and planets with effective temperatures below 2000 Kelvin.

Subject headings: infrared: stars — stars: fundamental parameters — stars: low mass, brown dwarfs, T dwarfs, spectroscopy, alkali metals, atmospheres, spectral synthesis

1. Introduction

Absorption lines of the neutral alkali metals sodium (Na), potassium (K), cesium (Cs), rubidium (Rb), and lithium (Li) are prevalent in the spectra of L dwarfs, T dwarfs, and irradiated giant planets (Kirkpatrick et al. 1999,2000; Burgasser et al. 1999,2000,2002; Burrows, Marley, and Sharp 2000 (BMS); Burrows et al. 2001,2002; Liebert et al. 2000; Charbonneau et al. 2001; Martín et al. 1999). The atmospheres of such substellar mass objects (SMOs) are cool enough that the neutral alkali atoms predominate. Furthermore, since aluminum, magnesium, iron, silicon, and calcium are sequestered in grains that have settled out, a cool atmosphere in the gravitational field of such

[1]Department of Astronomy and Steward Observatory, The University of Arizona, Tucson, AZ 85721; burrows@zenith.as.arizona.edu, maxim@as.arizona.edu

[2]Department of Chemistry, National Technical University, Kharkiv, Ukraine; maximnv@vbox.kharkov.ua

a planet or star is depleted of these more refractory metals (Burrows and Sharp 1999; Lodders 1999; BMS). As a consequence, the less-refractory neutral alkali metals assume an importance in the optical and near-infrared spectra of SMOs and in their atmospheres from ∼800 K to ∼2000 K that is unique among astronomical objects.

In standard stellar atmospheres, atomic lines are superposed on a background continuum and the concepts of equivalent width and curve of growth make conceptual and practical sense. An individual line is but a perturbation on the local spectrum. However, due to the rainout of metals in cool atmospheres and the consequent paucity of continuum and alternate opacity sources between 0.4 μm and 1.0 μm , the wings of the strong resonance doublets centered at ∼7700 Å (K I) and 5890 Å(Na-D) assume the role of the continuum throughout most of this spectral range (BMS; Tsuji, Ohnaka, and Aoki 1999). In particular, the red wing of the $4s^2S_{1/2} - 4p^2P_{3/2}$ transitions of K I provides the pseudo-continuum in cool molecular atmospheres all the way from 0.77 μm to ∼1.0 μm and the Na-D doublet, centered as it is in the middle of the visible, determines the true color of brown dwarfs (magenta/purple; Burrows et al. 2001).

Hence, whereas in traditional stellar atmospheres the Lorentzian core and Gaussian wings of a line are not generally of relevance beyond ∼20 Å detunings ($\Delta\lambda$ from the line core), in cool substellar atmospheres the relevant reach of the Na I and K I resonance lines can be thousands of Å. Given this, to achieve accurate spectral fits for brown dwarf, L dwarf, T dwarf, and hot giant planet atmospheres, the shapes of the far wings of these alkali lines as a function of pressure and temperature must be ascertained.

In this paper, we perform ab initio calculations of the energy shifts of the ground and excited states of sodium and potassium immersed in H_2- and helium-rich atmospheres and obtain the resulting opacity profiles of the red and blue wings of the Na-D and K I resonance lines. In §2, we review the general theory of line profiles in the quasi-static limit using the Unified Franck-Condon (UFC) formalism (Szudy and Baylis 1975,1996). In §3, we describe our use of the quantum chemical code GAMESS (Schmidt et al. 1993) to obtain the interaction potentials as a function of H_2 and helium perturber distance and H_2 orientation. The derived potential curves are presented and described in §4, where we also compare to related work in the literature. The resultant cross sections as a function of wavelength are given in §5. The latter section contains our major results. We compare our new theory with the approximate theories found in Burrows, Marley, and Sharp (2000) and Burrows et al. (2002) and find both similarities and important differences. In §6, we summarize our major conclusions.

2. Quasi-Static Theory of Absorption Spectra in the Far Wings of Atomic Spectral Lines

The energy levels of an atom of sodium or potassium immersed in a sea of molecular hydrogen will be perturbed by the potential field of the diatomic hydrogen. At a distance of R_i, the molecular

hydrogen will shift both the ground and the excited states of the alkali metal atom. The difference of these level shifts is the amount by which the corresponding absorption line will be shifted (Griem 1964; Breene 1957,1981):

$$h\nu = h\nu_0 + V_m(R_i) - V_n(R_i) = h\nu_0 + \Delta V_{mn}(= \Delta V)\,, \tag{1}$$

where ν is the photon frequency, ν_0 is the unperturbed photon frequency, m and n indicate the excited and ground states, and for an H_2 perturber the potential shifts V are a function of the orientation (angle) of the molecule and the distance. Note that $V_m(R_i)$ and $V_n(R_i)$ are the potential shifts with respect to the asymptotic shifts at infinity. ΔV is a central quantity in the quasi-static theory of line profiles.

The quasi-static theory of absorption strength assumes that the perturbers are arrayed about the transitioning atom in a static, thermal distribution with a density N_p given by its partial pressure and temperature (T) (Holtzmark 1925; Holstein 1950). A full quantum mechanical treatment of line shapes has been developed, but it has been applied to only a limited number of systems and is significantly more involved (Szudy and Baylis 1996). Fortunately, at least for the Na-He system, Pontius and Sando (1983) have shown that the semi-classical/quasi-static and the quantal methods yield very similar results.

In the quasi-static theory one imagines a shell of radius R_i and thickness dR_i centered at the atom. The strength of the absorption line in the wings at the frequency given by eq. (1) is then proportional to the number of perturbers in that shell:

$$4\pi R_i^2 N_p dR_i = \frac{4\pi R_i^2}{d\Delta V/dR_i} N_p d\Delta V\,. \tag{2}$$

The quantity $d\Delta V/dR_i$ has been extracted to show $d\Delta V$, which is proportional to the differential frequency ($d\nu$; eq. (1)). Eq. (2) indicates that the absorption cross section at frequency ν is proportional to:

$$\frac{4\pi R_i^2}{d\Delta V/dR_i} N_p e^{-\frac{V_0(R_i)}{k_B T}}\,, \tag{3}$$

where k_B is Boltzmann's constant, $V_0(R_i)$ is the ground state energy shift by a perturber at distance R_i, and the density of perturbers has been corrected by the corresponding thermal Boltzmann factor. Inverting eq. (1) to obtain $R_i(\nu)$ at a given absorption frequency yields an expression for the absorption cross section in the line wings at that frequency. Each solution for R_i at a given ν is called a Condon point, where the subscript i is now revealed to be the Condon point index. In principle, since ΔV can be multiple-valued, at a given frequency there can be multiple Condon points. Expressions like eq. (3) must be summed for all such points to obtain the total cross section.

Expression (3) is not only missing the dipole transition moment (oscillator strength f_{mn}), but is not normalized by the dipole (Thomas-Reiche-Kuhn) sum rule to yield the correct cross section $\sigma(\nu)$. Furthermore, it must be corrected at small detunings (large R_i). The correct expression for

the absorption cross section in the wings of a spectral line in the quasi-static approximation is given by the Unified Franck-Condon formula (Szudy and Baylis 1975,1996):

$$\sigma(\nu) = \sum_i \sigma_i(\nu) + \sum_{i,j=i+1} \sigma_{ij}(\nu)\,, \tag{4}$$

where

$$\sigma_i(\nu) = A\frac{R_i^2}{|\Delta V'(R_i)|}(\pi z_i)^{1/2}\left(L(z_i) + \frac{M(z_i)}{z_i}\right)e^{-\frac{V_0(R_i)}{k_BT}} \tag{5}$$

and

$$\sigma_{ij}(\nu) = 2A\frac{R_i^2}{|\Delta V'(R_i)\Delta V'(R_j)|^{1/2}}(\pi Z_{ij})^{1/2}\left(L(Z_{ij}) - \frac{M(Z_{ij})}{Z_{ij}}\right)e^{-\frac{V_0(R_i)}{k_BT}}\,. \tag{6}$$

A contains the transition oscillator strength and perturber number density and is given by:

$$A = 12\pi N_p \frac{\pi e^2}{m_e c^2} f_{mn}\,. \tag{7}$$

The arguments z_i and Z_{ij} are given by the expressions:

$$z_i = \frac{1}{2}\left(\frac{\mu}{k_BT}\right)^{1/3}\left(\frac{\Delta V'(R_i)}{\hbar}\right)^2\left|\frac{\Delta V''(R_i)}{\hbar}\right|^{-4/3} \tag{8}$$

and

$$Z_{ij} = \frac{1}{2}\left(\frac{\mu}{k_BT}\right)^{1/3}\left(\frac{\Delta V'(R_i)\Delta V'(R_j)}{\hbar^2}\right)\left|\frac{\Delta V''(R_i)\Delta V''(R_j)}{\hbar^2}\right|^{-2/3}\,, \tag{9}$$

where

$$\Delta V'(R_i) = \frac{\partial \Delta V}{\partial R_i} \tag{10}$$

and μ is the reduced mass of the interacting pair. $L(z_i)$ and $M(z_i)$ are functions defined through the integrals:

$$L(z_i) = \int_0^\infty d\zeta \zeta^{-2} Ai^2(-z_i\zeta)e^{-\zeta^{-3}} \tag{11}$$

and

$$M(z_i) = \int_0^\infty d\zeta \zeta^{-3} Ai'^2(-z_i\zeta)e^{-\zeta^{-3}}\,, \tag{12}$$

where $Ai(x)$ is the Airy function and $Ai'(x)$ is its derivative. The asymptotic behavior of $L(z_i)$ and $M(z_i)$ for positive z_i is:

$$L(z_i) = (36\pi z_i)^{-1/2} \tag{13}$$

and

$$M(z_i) = \left(\frac{z_i}{36\pi}\right)^{1/2}. \tag{14}$$

Eq. (5) is the expression that corresponds to eq. (3), the sum is over the Condon points (i and j), and $\sigma_{ij}(\nu)$ is the interference term between the Condon points. The interference term is

important only when $R_i \sim R_j$, at which point $\Delta V'(R_i)$ is formally zero. This singularity (seen in eqs. (3) and (5)) yields what is referred to as a "rainbow" or "satellite" feature (Beuc and Horvatic 1992) in the wings of an absorption spectrum. We expect such features in the Na I (5890 Å) and K I (7700 Å) absorption cross sections (§4 and §5). Note that at large z_i, the expression $(\pi z_i)^{1/2}(L(z_i)+\frac{M(z_i)}{z_i})$ in eq. (5) becomes a constant and eq. (5) reduces to eq. (3), modulo constants and the oscillator strength. Moreover, at large Z_{ij}, the expression $(\pi Z_{ij})^{1/2}(L(Z_{ij})-\frac{M(Z_{ij})}{Z_{ij}})$ in eq. (6) goes to zero.

The exponential terms in eqs. (5) and (6) provide natural cutoffs at positive (red) and negative (blue) detunings and depend only upon the ground-state potential shifts and temperature. Such cutoffs have been shown to be necessary for reasonable spectral fits to T dwarf spectra longward of ∼1.0 μm (Burrows et al. 2002) and are naturally provided by the quasi-static UFC theory.

The line cores (not the subject of this paper) are determined by distant encounters and are handled by assuming a van der Waals interaction potential with an adiabatic impact theory (Weisskopf 1933; Ch'en and Takeo 1957; Dimitrijević and Peach 1990), as in BMS and Nefedov, Sinel'shchikov, and Usachev (1999). The result is a pressure-broadened core of Lorentzian shape that applies out to only tens of wavenumber (cm^{-1}) detunings. The major contribution to the alkali line profile shape is determined by the statistical UFC theory, which applies beyond the core to thousands of wavenumber (and thousands of Angstrom) detunings. The procedure for obtaining the wing absorption profiles is first to calculated the potential curves for the relevant levels of Na and K (§3 and §4), then to calculate the Condon points, and finally to employ eq. (4). We do this for Na+H_2, Na+He, K+H_2, and K+He interaction pairs, and for the states that contribute to both the red and the blue wings of the 5890 Å and 7700 Å resonance features. For perturbations by H_2, the potential interactions are functions of angle (orientation), introducing yet another degree of complexity.

3. Technique for Calculating the Interaction Potentials and Line Shifts

The Na-D doublet of neutral sodium involves the $3s^2S_{1/2} - 3p^2P_{3/2,1/2}$ transitions, where the D_2 transition (5890 Å) is from the 1/2 state to the 3/2 state with a multiplicity of 4 ($= 2j + 1$) and the D_1 transition (5896 Å) is from 1/2 to 1/2 with a multiplicity of 2. Hence, the ratio of the D_2 and D_1 line strengths is 2. The analogous transitions for potassium are $4s^2S_{1/2} - 4p^2P_{3/2,1/2}$ at 7665 Å and 7699 Å, respectively, with a similar strength ratio. Since the upper states of the D_2 transitions are $j = 3/2$ states, they include p_x and p_y states that in molecular orbital theory can form bonding states with H_2 (oriented perpendicularly). The p_z state associated with the $^2P_{1/2}$ state is anti-bonding to H_2. Figure 1 depicts the orientations of the interacting H_2 and Na pair for C_{2v} symmetry (H→H line perpendicular to the Na-H_2 line). The potassium $4p$ states can be depicted in a perfectly analogous way. The $^2A_1$ states depicted in Fig. 1 are anti-bonding and the interaction potential is purely repulsive at all distances R_i. The $^2B_{1,2}$ states are attractive at large

distances and repulsive at small distances [3]. The ground states of both the Na+H_2 and the K+H_2 systems are repulsive for all distances R_i. The upshot is that the energy difference between the ^{2}B state of the D_2 transition and the ground state decreases with decreasing R_i until R_i is quite small. Hence, the D_2 line, though it is blueward of the D_1 line for atoms in isolation, provides the red wing of the alkali line. Correspondingly, the D_1 line provides the blue wing.

A schematic of the excited-state minus ground-state energy shifts of the Na-D and K I resonance lines is given in Fig. 2. Figure 2 depicts the mapping between energy shift, line core, red wing, and blue wing. Note that ΔV on the blue wing has a maximum (extremum), which results in a rainbow satellite feature. The absence of a corresponding extremum on the red wing means that there is no corresponding satellite feature redward of the line core.

To calculate the interaction potentials, we employ the multi-configurational self-consistent-field (MCSCF) variant of the quantum chemical code GAMESS (Schmidt et al. 1993). The Hartree-Fock (HF) method is a self-consistent field approach that employs iteration to find a consistent solution to the multi-electron, multi-nucleus wavefunction (itself a Slater determinant), but assumes that the potential is a smoothed average and does not explicitly include electron-electron interactions. MCSCF is a post-HF method that includes electron-electron interactions and exchange forces, the so-called configuration interaction (CI), but assumes that the CI term is small. It allows variation of not only the mixing coefficients of the various HF configurations, but also of the coefficients of the basis functions in the constituent molecular orbitals. In this way, the HF orbitals from which the total wavefunction is constructed are optimized simultaneously. The MCSCF method requires care in the selection of the basis set, but generally achieves a good solution for problems having low-lying excited states, as in the problem at hand. We use the Complete Active Space Self-Consistent Field (CASSCF) version of MCSCF and the 6-31G** split-valence basis set that incorporates Gaussian Type Orbitals (GTO) (Frisch et al. 1998). In practice, we first obtain a solution with the HF method, and then use this solution as a first guess in the full MCSCF/CASSCF calculation. This two-step approach has often proven necessary to achieve converged solutions.

We use the above methods and the GAMESS code to solve the many-electron Schrödinger equation for the wavefunctions and the energy levels of the various electronic states as a function of distance R_i for the composite system of alkali metal atom and either H_2 or helium. For H_2, this is done for a variety of orientations (from C_{2v} [$\theta = 90°$] to C_∞ [$\theta = 0°$] (parallel) symmetries) and we keep the H–H bond length constant (Botschwina et al. 1981). We have included electron correlation effects successfully for He perturbations and for H_2 perturbations germane to the red wings of both the Na and K lines. However, when calculating the blue wings for orientation angles other than 0° or 90° we had difficulty obtaining converged solutions with the electron correlation effects (CI) included. Hence, for the blue wings of the Na/K+H_2 interaction pairs we have settled for the pure Hartree-Fock solutions. This approximation is good for large R_i, but begins to break

[3]Note that in order to connect to both communities, we use both the spectroscopist's (A and B) and the physicist's ($P_{1/2,3/2}$) nomenclature for the states.

down at small R_i and large detunings.

For all the relevant ^2A and ^2B states we calculate the interaction potentials as a function of both distance and (for H_2) angle of orientation. The calculations are done at hundreds of distances and (for H_2) for five angles ($\theta = 0°, 20°, 45°, 70°$, and $90°$). Then, we calculate the energy shifts (ΔV) of the resonance transitions of Na and K. Though we reproduce the wavelengths of the isolated D_2 and D_1 lines of Na to within ∼14% (0.3 eV) and for K to within ∼21% (0.34 eV), we shift our calculated energy shifts by a constant amount that ensures that the line shift at very large R_i is zero. This puts the line core exactly at the measured wavelength by construction. Furthermore, we do not calculate the dipole transition matrix elements as a function of R_i, but use the published oscillator strengths of the unperturbed Na and K resonance doublets in the calculation of the line profiles (eq. 7). These incorporate the 2:1 strength ratio due to the spin degeneracy of the final states in the unperturbed D_2 and D_1 transitions.

4. Potential Curves for the Na+H_2, K+H_2, and Na/K+He Systems

Figure 3 depicts the energy levels as a function of separation of the various states (relative to the ground state at infinite separation), for both Na and K perturbed by both helium and H_2. For H_2, the run of energy shift with R_i for the four states is given for various orientation angles. As Fig. 3 shows, the ground state interaction is always repulsive and is most repulsive for H_2 for colinear orientations (C_∞ symmetry). This is the $V_0(R_i)$ term to be used in eqs. (5) and (6) in calculating the cutoff exponential. The ^2B states associated with the p_x and p_y atomic orbitals of sodium or potassium show a slight attraction for large angles (close to perpendicular) and large distances, but then become universally repulsive as the hard core is approached (Botschwina et al. 1981). Figure 4 portrays the resulting transition energies for the D lines of both Na and K as a function of separation and angle. As is clear from the figure, the energy differences for the transitions for which the excited states are ^2B states decrease with decreasing separation and, hence, are associated with the red wings of the spectral lines. Similarly, since the ground-state to $^2A_1$-state transitions have the opposite behavior, they are associated with the blue wings. Furthermore, the peaks seen at the bottom of Fig. 4 at separations of $R_i \sim 2.4 - 2.5$Å and $R_i \sim 3.1 - 3.2$Å, respectively, for Na and K perturbed by H_2 imply that their blue wings have satellites at wavelengths of ∼0.49-0.5 μm and ∼0.66–0.68 μm. The K satellite might be near the Li feature at 6708 Å. Fig. 2 schematically shows how the panels of Fig. 4 merge to make the corresponding absorption profiles.

It is useful to compare these potential calculations with previous related work using different methods. Rossi and Pascale (1985, RP) have done l-dependent pseudopotential calculations for the Na+H_2 and K+H_2 systems and Botschwina et al. (1981) have done RHF-SCF and PNO-CEPA calculations for the Na+H_2 system. The PNO-CEPA potential curves of Botschwina et al. are similar to those of RP. Neither did the calculations for the arbitrary H_2 orientations and small separations necessary to perform the line profile calculations that motivated this paper. Rather, they concentrated solely on separations greater than 2.0 Å and on the C_∞ and C_{2v} symmetries.

Nevertheless, their potential curves for these symmetries are similar to those found in Fig. 3. For C_{2v} symmetry and the Na+H_2 system, RP derive that the potential minimum for the $^2B_1$ state is at 2.4 Å and has a depth of 0.12 eV; we obtain 2.45 Å and 0.1 eV. For the $^2B_2$ state, RP derive corresponding numbers of 2.12 Å and 0.35 eV; we obtain 2.27 Å and 0.2 eV. For the K+H_2 system, RP derive for the $^2B_2$ state a minimum at 3.0 Å with a depth of 0.49 eV; we obtain 3.0 Å and 0.5 eV. RP estimate that the change in the potential of the $^2A_1$ excited state of the Na+H_2 system with C_{2v} symmetry in going from 4.0 Bohr radii (2.12 Å) to 8.0 Bohr radii (4.23 Å) is 0.55 eV; we obtain 0.7 eV. Furthermore, Kleinekathöfer et al. (1996), who use a surface integral method to derive the ground-state potential curve of the Na+He system, derive $V(R_i = 3.2 \text{ Å}) = 0.10$ eV; we obtain 0.08 eV at the same distance. All in all, our results compare favorably with those in previous studies, with the Na+$H_2/^2B_1$ and K+$H_2/^2B_2$ potential curves corresponding most closely. However, the correspondences are not perfect and we sometimes see discrepancies of as much as ∼0.1 eV at a given separation. We suspect that these discrepancies are traceable either to our choice of basis sets or to the MCSCF assumption that the CI term is small.

Since the second derivative of the potential (V'') is needed when using eqs. (5) and (6) to obtain the satellite profile shapes, small errors in the potential calculations when $V' = 0$ can be amplified at the rainbow positions. Ch'en and Wilson (1961) measured the "violet band separation" for the satellite features on the blue wings of the Na+He and the K+He systems to be 1161±15 cm^{-1} and 838±5 cm^{-1}, respectively, which translate into satellite positions at 0.55 μm and 0.72 μm . These contrast with the satellite positions we derive of 0.515 μm and 0.69 μm , respectively, for perturbation by helium. Not unexpectedly, the centers of the satellite features are the most poorly determined quantities in our theory. We now turn to the calculation of the opacity profiles in the wings of the D_2 and D_1 lines of Na and K due to perturbations by H_2 and helium using the potential curves represented in Figs. 3 and 4.

5. The Absorption Cross Sections on the Red and Blue Wings of the Na (5890Å) and K (7700Å) Resonance Lines

Using the UFC/quasi-static eqs. (5) and (6), we obtain the absorption spectra as a function of photon wavelength for the D_2 and D_1 lines of Na and K centered near 5890 Å (0.589 μm) and 7700 Å(0.77 μm), respectively. These are depicted in Fig. 5 at a temperature of 1000 K and a total pressure of one atmosphere. The contributions at various orientation angles of H_2, the angle-integrated spectra (solid), and the results for the Na+He and K+He systems are shown. The Lorentzian cores are not included on this plot. Since the ground-state potential shift increases quickly at small separations (Fig. 3), and the associated exponential terms in eqs. (5) and (6) introduce a large cutoff, Condon points at such small separations make only a marginal contribution to the overall opacities. As a consequence, though there can be more than two Condon points (Fig. 4), we include at most the outer two in our theory. For the same reason, we ignore possible satellites on the very far red wings.

Figure 5 encapsulates the central results of our study. The cutoff on the red wing of the potassium feature due to the exponential term (eq. 5) containing the ground-state interaction potential of the K+H_2 system is seen to be situated between 0.95 μm and 1.0 μm , close to the 0.98 μm used in Burrows et al. (2002). The cutoff of the red wing of the Na feature is near 0.8 μm , but is a bit more gradual. The corresponding cutoffs for the alkali-He systems are more abrupt, but of less importance due to the lower abundance of helium. It should be noted that for the temperatures in cool atmospheres the precise form and position of this cutoff is a sensitive function of the ground-state potential. Errors in the potential of $\lesssim$0.1 eV that may arise at small R_i for the alkali-H_2 systems translate directly into shifts in the position of the turnover and in the magnitude of the cross section at the turnover. Such an effect is demonstrated by the difference between the cross sections with and without electron-correlation/configuration-interaction terms (depicted below in Fig. 7). Figure 5 also makes clear that the red and blue wings are asymmetrical, as one would expect from the discussion in §4 and Fig. 4.

The satellite features identified on the blue wings of both the Na and K features by the asterisks on Fig. 5 have been alluded to before, but we note once again that our calculations are too imprecise to derive the detailed shape of the actual rainbow structures (which for the alkali-H_2 systems is a composite of the corresponding curves for the various angles). Nevertheless, the existence and approximate wavelengths of the satellites remain clear.

Figure 6 portrays the temperature and pressure dependences of the line profiles. Three curves (at 800, 1000, and 1500 K) show the temperature dependence at one atmosphere pressure and one curve at 1000 K and 10 atmospheres shows, by comparison with the other 1000 K curve, the pressure dependence. Due to the N_p dependence in eq. (7), higher pressures lead to higher wing strengths. The Thomas-Reiche-Kuhn sum rule is still satisfied by a corresponding diminution in the strength in the Lorentzian core. Due to the exponential term, increasing the temperature raises the cross section in the far wings. However, due to the constraint of constant pressure, increasing the temperature slightly lowers the cross sections in the near wings.

It should be emphasized that, unlike the theory of BMS, and the line profile formalism used in Burrows et al. (2002), there are no free parameters in our theory. The cutoffs and shapes arise naturally because the physics of the line-broadening process has been treated. Limitations on the accuracy of the current work are in the accuracy of the quantum chemistry calculations of the potential curves and in the use of the semiclassical formalism to treat the broadening. The earlier theory of BMS was constructed to fill the theoretical and experimental void concerning the far wing profiles of the alkali metal lines perturbed by molecular hydrogen. Burrows et al. (2002) followed with a simpler theory that used a Gaussian-truncated Lorentzian profile. Previously in astrophysics the character of the far wings of the K I and Na D resonance features perturbed by H_2 had not been needed.

Given our new calculations, it is useful to compare them with the stopgap theories of BMS and Burrows et al. (2002). Figure 7 is a comparison of the BMS (red) and Burrows et al. (2002)

(green) potassium cross sections with the corresponding cross sections using the theory of this paper (blue). For the BMS prescription, we arbitrarily set the associated q parameter equal to 0.5. A temperature of 1000 K and a pressure of one atmosphere were assumed. The BMS and the Burrows et al. (2002) curves include the Lorentzian core, while the newly-calculated quasi-static curve does not. Also shown are the new cross sections calculated without the configuration interaction (CI) (blue, dashed). At the inner red wing, the theory of Burrows et al. (2002), in which the pressure-broadened Lorentzian was truncated with a Gaussian near 0.98 μm , is within a factor of three of the more detailed calculation, but clearly deviates from it. However, on the red wing the simple theory of BMS is actually surprisingly close to the new result. On the far red wing, the cross sections of the new theory plummet more precipitously than either BMS or Burrows et al. (2002). This emphasizes even more strongly the existence of the steep cutoff inferred by Burrows et al. (2002) to be necessary in order to reproduce the Z ($\sim$ 1.0 μm) and J ($\sim$ 1.2 μm) band fluxes observed for the T dwarfs (Burgasser et al. 2002). Note, however, that the new cross sections on the far blue wing are as much as a factor of four higher than the corresponding cross sections of the old theories. The same result obtains for the blue wing of the Na-D line. In sum, though the BMS theory was good in the near red wings, in places the contrast between both the BMS and the Burrows et al. (2002) formulations and our parameterless UFC calculations is large. As a result, we recommend that in the future the new theory be used for detailed T and L dwarf spectral calculations.

6. Conclusions

Using the quantum chemical code GAMESS, we have calculated as a function of distance the interaction potentials of the excited and ground states of sodium and potassium perturbed by H_2 and helium. For H_2, we also calculated the dependence of the interaction potentials on orientation angle. Using these potentials and the Unified Franck-Condon formalism, we derived the absorption line profiles in the wings of the Na-D doublet and the K I resonance doublet at detunings of thousands of Angstroms. These lines and their wings are of central importance in the atmospheres and spectra of brown dwarfs, T dwarfs, L dwarfs, and hot Jupiters. Our theory has no free parameters and naturally accounts for the cutoffs in the far red wings inferred to be present to explain the high J and Z band fluxes observed in T dwarfs (Burrows et al. 2002). However, the new cross sections differ from those used previously by having sharper cutoffs, stronger blue wings, and satellite features. Furthermore, the red/blue asymmetry is pronounced.

From our calculations using the full configuration interaction at the subset of useful H_2 orientation angles for which we were able to obtain convergence for the $^2A_1$ states (of relevance for the calculation of the blue wings) and from a comparison of the Hartree-Fock and CI results for perturbations by helium, we have determined that the HF and CI numbers on the blue wings differ little, though the associated potential differences on the red wings can differ by $\sim$0.1 eV. This gives us some confidence that, despite the fact that we use the HF approach on the blue wings

for perturbations by H_2, our blue wing results are satisfactory. Fortunately, for all the red wing results, we were able to obtain full convergence using the MCSCF/CI formalism at all H_2 angles.

The need for line wing strengths at such large detunings has few precedents in astrophysics. The next step is to incorporate the new alkali line opacities into a spectral synthesis code and to identify the differences between the fits using the old and the new algorithms. The line cores will be unchanged, but the blue wings and the spectra from 0.8 μm to 0.9 μm on the red wings of the K I line will be slightly altered, as else being equal. The major virtue of our new algorithm is that it is parameterless. As a result, we reduce by one (or even a few) the number of free parameters needed in fits to the increasing number of optical and near-IR spectra being measured for T dwarfs (in particular), thereby making the extraction of physical quantities such as effective temperature and gravity more robust and reliable.

We are happy to thank Ludwik Adamowicz, Jonathan Lunine, Christopher Sharp, David Sudarsky, and Bill Hubbard for help, advice, and useful discussions. This work was supported in part by NASA grants NAG5-10760, NAG5-10629, NAG5-7499, and NAG5-7073 and with the help of JPL contract # 1241086 under the NASA Navigator program. Tables of our potential curves are available from the first author upon request.

REFERENCES

Anders, E. and Grevesse, N. 1989, Geochim. Cosmochim. Acta, 53, 197

Beuc, R. and Horvatic, V. 1992, J. Phys. B: At. Mol. Opt. Phys., 25, 1497.

Botschwina, P., Meyer, W., Hertel, I., Reiland, W. 1981, J. Chem. Phys., 75, 5438

Breene, R.G. Jr. 1957, Rev. Mod. Phys., 29, 94

Breene, R.G., Jr. 1981, "Theories of Spectral Line Shape," (New York: John Wiley), p. 344

Burgasser, A.J., et al. 1999, ApJ, 522, L65

Burgasser, A.J., Kirkpatrick, J. D., Reid, I. N., Liebert, J., Gizis, J. E., & Brown, M. E. 2000, AJ, 120, 473

Burgasser, A.J., et al. 2002, ApJ, 564, 421

Burrows, A. and Sharp, C.M. 1999, ApJ, 512, 843

Burrows, A., Marley, M. S., and Sharp, C. M. 2000, ApJ, 531, 438

Burrows, A., Hubbard, W.B., Lunine, J.I., and Liebert, J. 2001, Rev. Mod. Phys., 73, 719

Burrows, A., Burgasser, A.J., Kirkpatrick, J.D., Liebert, J., Milsom, J.A., Sudarsky, D., and Hubeny, I. 2002, ApJ,, 573, 394

Ch'en, S.Y. and Takeo, M. 1957, Rev. Mod. Phys., 29, 20

Ch'en, S.Y. and Wilson, R.A. 1961, Physica, 27, 497

Dimitrijević, M.S. & Peach, G. 1990, A&A, 236, 261

Frisch, M.J. et al. 1998, Gaussian, Inc., Pittsburgh, PA (http://www.gaussian.com/citation.htm)

Griem, H.R. 1964, "Plasma Spectroscopy," (New York: McGraw Hill)

Holstein, T. 1950, Phys. Rev., 79, 744

Holtzmark, J. 1925, Z. für Physik, 34, 722

Kirkpatrick, J.D., Reid, I.N., Liebert, J., Cutri, R.M., Nelson, B., Beichman, C.A., Dahn, C.C., Monet, D.G., Gizis, J., and Skrutskie, M.F. 1999, ApJ, 519, 802

Kirkpatrick, J. D., Reid, I. N., Liebert, J., Gizis, J. E., Burgasser, A. J., Monet, D. G., Dahn, C. C., Nelson, B., & Williams, R. J. 2000, AJ, 120, 447

Kleinekathöfer, U., Tang, K.T., Toennies, J.P., and Yiu, C.L. 1996, Chem. Phys. Lett., 249, 257

Liebert, J., Reid, I. N., Burrows, A., Burgasser, A. J., Kirkpatrick, J. D., & Gizis, J. E. 2000, ApJ, 533, L155

Lodders, K. 1999, ApJ, 519, 793

Martín, E. L., Delfosse, X., Basri, G., Goldman, B., Forveille, T., & Zapatero Osorio, M. R. 1999, AJ, 118, 2466

Nefedov, A.P., Sinel'shchikov, V.A., and Usachev, A.D. 1999, Physica Scripta, 59, 432

Pontius, E.M. and Sando, K.M. 1983, Phys. Rev. A, 28, 3117

Rossi, F. and Pascale, J. 1985, Phys. Rev. A, 32, 2657

Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.J., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M., Montgomery, J.A. 1993, J. Comput. Chem., 14, 1347

Szudy, J. and Baylis, W. 1975, J. Quant. Spectrosc. Radiat. Transfer, 15, 641

Szudy, J. and Baylis, W. 1996, Physics Reports, 266, 127

Tsuji, T., Ohnaka, K., and Aoki, W. 1999, ApJ, 520, L119

Weisskopf, V. 1933, Z. für Physik, 43, 1

AAS LaTeX macros v5.0.

Fig. 1.— Relative orientations of the hydrogen molecule and the electron cloud of the sodium atom in the ground (3s) and excited ($3p_x$, $3p_y$, $3p_z$) states. For the C_{2v} symmetry (H_2 orientation perpendicular to H_2-Na line) of the Na+H_2 complex, all the excited electronic states have different energies $E(3p_x) < E(3p_y) < E(3p_z)$, but for the C_∞ symmetry (all atoms colinear, not shown) the B_1 and B_2 states are degenerate. The B states map onto the red wing, while the A state maps onto the blue wing. The corresponding figure for potassium is quite similar, but involves 4s and 4p states.

Fig. 2.— A schematic of the relationship between the interparticle distance R, the excitation energy ΔV, and the spectrum. Large shifts away from the atomic line center are associated with small distances where the chemical interaction is strongest. The rainbow satellite feature appears at the radius (frequency) at which the excitation energy is maximum. Satellites are observed in the systems of concern in this paper only on the blue wings.

Fig. 3.— Interaction potentials (in eV, relative to zero at infinity) for all states of the Na+H_2 and K+H_2 systems as a function both of the separation (R, in Å) and of the angle of orientation of the H_2 molecule with respect to the line between the alkali metal atom and the molecule. The similar electronic structures of Na and K lead to similar shapes and behaviors for the curves. The A_1 states (including the ground state) are repulsive for all separations, while the excited ^2B states can be attractive for a range of separations and angles. Also included (long dash) are the corresponding curves for perturbations by helium.

Fig. 4.— Energy shifts (ΔV, in eV) relative to the ground states for the Na+H_2 and K+H_2 complexes as a function of separation (R, in Å). The energy differences for the transitions to the excited $^2P_{3/2}$ (^2B) states are below those for the isolated D atomic lines (at 2.1 eV for Na and 1.6 eV for K) and, hence, are associated with the red wings of the spectra. The corresponding curves for the excited $^2P_{1/2}$ (^2A) states are above those for the isolated D lines and, hence, are associated with the blue wings of the absorption spectra. The extrema seen in the bottom panels associated with the blue wings mean that the blue wings have satellites. The corresponding curves for perturbations by helium are also shown (long dashed).

Fig. 5.— Absorption cross sections (in cm^2) versus wavelength (in μm) for the Na-D and K I doublets at 5890 Å and 7700 Å, respectively, using the quasi-static theory of wing line profiles. The Lorentzian line cores are not included on this plot. Cross sections are shown for the different orientations of the H_2 molecule ($\theta = 0°, 20°, 45°, 70°, 90°$), as well as after integrating over angle (solid). The behavior is monotonic with angle, from steepest (small angle) to shallowest (large angle). Also depicted are the cross sections due to perturbations by the spherical helium atom (with C_∞ symmetry). The asterisks indicate the positions of the rainbow satellites on the blue wings. Due to resolution problems with the potential calculations (which are amplified when using eq. (6) for which the second derivative V'' is needed), we have not attempted to obtain the precise shape of the satellite features. A temperature of 1000 K and a total pressure of one atmosphere have been used. The partial pressure of He is assumed to be ∼10% of this total (Anders and

Grevesse 1989).

Fig. 6.— Representative temperature and pressure dependences of the absorption cross sections for the Na/K + H_2 systems. At one atmosphere pressure, cross sections (in cm^2) at temperatures of 800 K (blue), 1000 K (red), and 1500 K (green) are depicted. Another curve at a pressure of 10 atmospheres and a temperature of 1000 K is shown (purple). The left ends terminate at the central positions of the satellites. Note that the positions of these rainbow features are very weak functions of pressure and temperature and that the cutoff wavelength on the red wings (however defined) is an increasing function of temperature.

Fig. 7.— A comparison at a temperature of 1000 K and a pressure of one atmosphere of the potassium absorption cross sections used in Burrows, Marley, and Sharp (BMS, 2000) (red) and Burrows et al. (2002) (green) with those derived in this paper using the UFC theory (blue). For the BMS curve, a q parameter equal to 0.5 is used. The dashed curve (blue) is the absorption cross section derived neglecting electron correlation (configuration interaction, CI) effects. The asterisk near 0.66 μm marks the approximate position of the K+H_2 satellite.